NBSIR 80-2158

Some Considerations Regarding Film Thickness Standards for the Semiconductor Industry

James R. Ehrstein

Electron Devices Division
Center for Electronics and
Electrical Engineering
National Bureau of Standards
U.S. Department of Commerce
Washington, DC 20234

November 1980

DEPARTMENT OF COMMERCE
NAL BUREAU OF STANDARDS

NBSIR 80-2158

SOME CONSIDERATIONS REGARDING FILM THICKNESS STANDARDS FOR THE SEMICONDUCTOR INDUSTRY

James R. Ehrstein

Electron Devices Division
Center for Electronics and
Electrical Engineering
National Bureau of Standards
U.S. Department of Commerce
Washington, DC 202340

November 1980

U.S. DEPARTMENT OF COMMERCE, Philip M. Klutznick, *Secretary*

Jordan J. Baruch, *Assistant Secretary for Productivity, Technology and Innovation*

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

SOME CONSIDERATIONS REGARDING THIN FILM STANDARDS
FOR THE SEMICONDUCTOR INDUSTRY

ABSTRACT

Semiconductor integrated circuit manufacturing has witnessed a rapid evolution of processing techniques and a reduction of structural dimensions. This has placed a great burden on metrology for process development and for process monitoring, both because of the smallness of the dimensions involved and the variety of interferences encountered in measuring differing structural combinations of thin films. One possible means for improving the uniformity and control of semiconductor thin film measurement would be through the use of certified thickness standards, such as have been requested of the Standard Reference Material Program at the National Bureau of Standards.

This paper will first consider some of the requisite properties of Standard Reference Materials (SRMs) for effective use in improving the uniformity of measurements. It will then consider some of the limitations imposed by real-world thin film specimens and our state of understanding of their properties as well as by the different types of measurements available. Finally, the need for improved measurement control will be related to the SRM program in light of these limitations.

Key words: Ellipsometry; polysilicon films, Standard Reference Materials; silicon dioxide films; silicon nitride films; thin films.

SOME CONSIDERATIONS REGARDING THIN FILM STANDARDS FOR THE SEMICONDUCTOR INDUSTRY

James R. Ehrstein
Electron Devices Division
National Bureau of Standards
Washington, DC 20234

The certification and dissemination of Standard Reference Materials is one of several approaches taken by the National Bureau of Standards to improve measurement accuracy and compatibility in both laboratory and industrial environments. It is the purpose of this paper to relate the concepts of Standard Reference Materials to the emerging need within the semiconductor industry for film thickness standards. The comments made are particularly directed to dielectric layers with thickness of 100 nm or less, i.e., to present and future MOS gate dielectric layers, since these seem to be the category of semiconductor dielectrics most in need of control and measurement accuracy.

A reference material is a physical artifact which has been carefully measured, certified for value(s) of one or more properties, and issued by a laboratory whose reputation for careful metrology gives credibility to the certified value(s). The National Bureau of Standards is but one of a number of national and private laboratories around the world which issue certified reference materials. Those materials issued by NBS are generically called Standard Reference Materials (SRMs). Standard Reference Materials are used in a metrological hierarchy to provide a transferable link to the basic standards of mass, length, time, etc. They are discussed as part of a systems approach to measurement compatibility by Uriano and Gravatt [1]. The function of SRMs is to facilitate transfer of measurement scales between better types of measurements, instrumentation, and procedures and those which are less rigorous. In the case of measurements in engineering applications, it is often desirable to have available sets of standards at two, three, or more values. Multiple level sets serve to check for gain, fixed point, and linearity of response of a measurement scale. Their effectiveness may be diminished, however, if the measurement or instrument utilizing the SRM offers no means for adjusting linearity, gain, and fixed point (or comparable functions) to match the scale of the SRMs.

Whenever possible, SRMs are certified on the basis of accuracy; that is, the certified value is the best estimate of the "true value." This aspect of accuracy is of primary importance because there are legal aspects to certification: the full weight and authority of NBS and the U.S. Department of Commerce are implied. Further, the logical necessity for stressing accuracy can be readily recognized if one envisions the use of SRMs to arbitrate conflict in the marketplace. Such conflict could arise between a buyer and seller who disagree about the value of one of the attributes of the seller's product, and who resort to an appropriate SRM to test their abilities to measure that attribute accurately. In a similar fashion, the conflict could be between competing suppliers of the same or similar products or instruments, each trying to demonstrate the quality or superiority of his product, and enlisting the use of SRMs to test that quality.

It is preferred that SRMs be measured and certified through the use of "definitive" measurement methods, i.e., methods that produce precise numerical values free from, or correctable for, all sources of systematic error. This requires a complete measurement theory with minimal (or no) model assumptions and a full understanding of the apparatus being used. "Definitive" methods, if they exist for the measurement of interest, allow the property being measured to be traced back to the basic standards of mass, length, etc., or to natural constants (e.g. the velocity of light). However, most analytical methods cannot be classified as definitive because no complete theory relates all the experimental variables to the final result. When definitive methods are not available, use of one or more "reference" methods, which are well documented as to procedure and quality of results obtainable, are used for SRM certification. The design and use of such methods must include careful consideration of systematic errors, but the methods may be more heavily dependent on models for interpretation than is desirable. As a result, the SRM certification values are often test-method-dependent. (Many of the methods documented in the Annual Book of Standards of the American Society for Testing and Materials [2] can be classed as reference methods.) After SRMs are certified, whether by definitive or reference methods, they can aid the overall measurement process only through careful adherence to measurement procedures given on the certificate as well as to other factors such as sampling and storage procedures. These latter precedures relate to inevitable questions of uniformity and stability in any physical system.

In the best of situations an SRM, in this case an SRM for dielectric thickness, would carry with it an accurate statement of the thickness of the dielectric in the SRM. It would be useful for calibrating, or transferring, a thickness scale to a variety of thickness measuring techniques and the thickness scale so derived could be validly applied or transferred in turn to a variety of dielectric layers of the user's choice, which may or may not have been fabricated by the process used for the SRM. In this best of situations, both accuracy (for any one measurement technique) and uniformity of measurement response (among various possible techniques) could be achieved through use of the SRM.

As will be discussed, limitations and variations in real dielectric layers, differences in the available measuring techniques (not all of which are understood), and lack of complete control of the measurement processes preclude the achievement of the desired measurement accuracy and uniformity for all applications. It is nevertheless possible to improve on the status quo by making a judicious compromise between accuracy and overall uniformity of measurement through an SRM certification process which allows measurement scale transfer, but is restricted as to technique or application. Limitations on film thickness measurements are imposed by certain known properties of the materials involved as well as by lack of perfect quantitative knowledge about other important properties. For simplicity, the discussion will begin with thermally grown silicon dioxide layers.

Layers of silicon dioxide on silicon are simple, yet not ideal, structures. As has been shown by numerous authors, e.g., [3,4], a sharp change in stoichiometry from silicon dioxide to silicon does not occur. An interface layer with graded composition and having thickness which depends on the oxide growth process separates the silicon dioxide and silicon regions. The struc-

tural difference between silicon and its oxide is expected to cause strain and optical birefringence in the oxide. Further, as will be shown in the appendix, the oxide layer is subject to contamination and apparent growth in any reasonable storage environment. Whether these effects cause serious errors depends on what is required from the SRM in terms of application, precision, and accuracy.

One can readily envision that accurate metrology becomes rapidly more difficult in the case of multiple layer dielectrics such as the nitride-oxide double layer used in MNOS structures. Errors caused by transition regions and layer strain now occur in each dielectric layer, and the ability to make accurate measurements and standards is degraded. This situation may be further complicated by the variety of processes available for fabricating single or multiple dielectric layers since it has yet to be shown that the magnitude of transition layers, of strain, and of other effects is comparable for the various processes.

Of the measurements available for dielectric layer SRM certification, an optical technique appears preferable both because it can be performed nondestructively and because optical measurements are in common use in the industry. Multiple-beam (Tolansky) interferometry is perhaps the best candidate in the definitive technique category, but it requires metallization over a step etched in the dielectric and more importantly, has limited resolution imposed by the smallest fraction of an interference fringe which can be counted. Ellipsometry, although not a definitive measurement of thickness, has much better resolution and is perhaps the best compromise candidate technique for certifying SRMs for dielectric thickness. This method has been extensively documented regarding procedure, instrumentation errors and data analysis [5,6] to qualify it for use as a reference method. Further, an ASTM Standard Method specifies the use of ellipsometry for measuring dielectric layer thickness [7].

In ellipsometry the dielectric layer thickness is not measured directly, but rather the phase difference and transmission ratio for two polarized beams are measured. Using the Fresnel reflection equations for these beams and assuming a model based on a sharp transition between two layers, an effective top layer thickness and index of refraction are derived. In fact, owing both to nonideality of ellipsometric optical components and imprecision in measured values, the solutions for thickness and index are not unique although the resulting uncertainty can generally be made quite small [6]. Effects due to strain in the oxide can be estimated and corrected for, and the effects of a graded interlayer between silicon dioxide and silicon can be approximately accounted for by using Fresnel equations for a three- (or more) layer model. In this case, the additional layers in the model are used to account for the graded physical interlayer [4].

A further complication in ellipsometer measurements arises from the fact that the optical properties of the silicon substrate affect the ellipsometer results. Sufficient scatter exists in the reported value of silicon optical constants [8] to have a noticeable effect on the oxide layer thickness and refractive index values which are calculated from any given set of ellipsometer data. This is illustrated in figure 1, which shows the range of thickness and index values obtainable for silicon dioxide layers from the same set

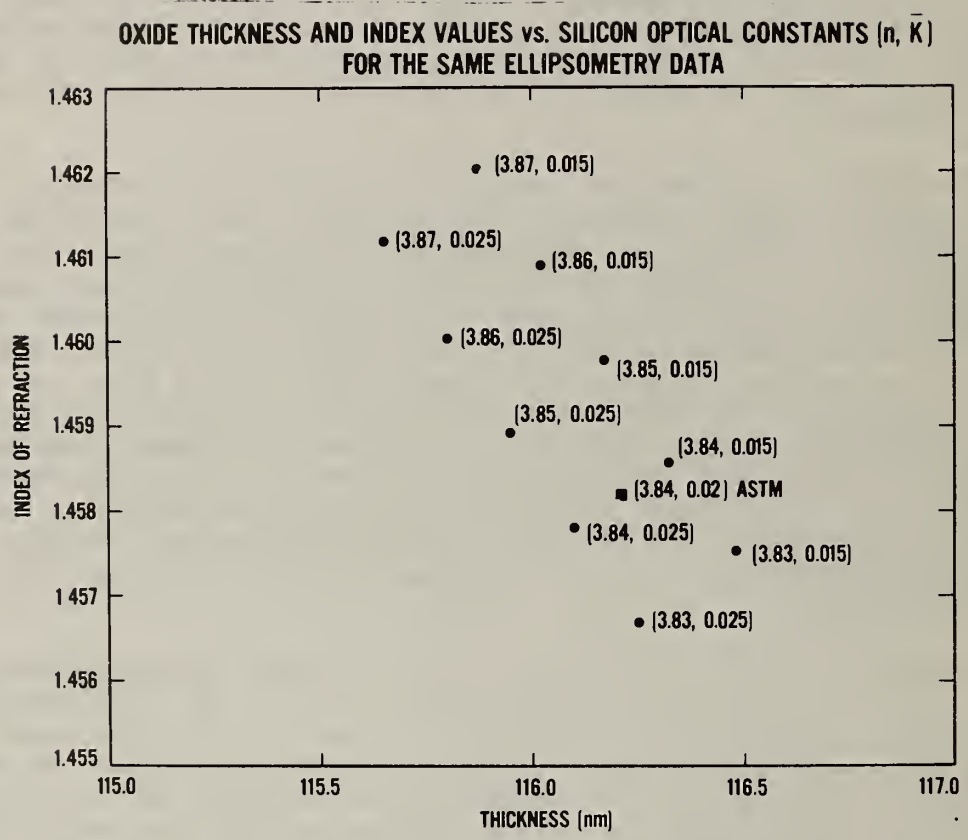

Figure 1. Silicon dioxide thickness and refractive index values calculated from a single set of ellipsometry data by using various silicon optical constants (n,k).

of ellipsometry data using the analysis program of McCrackin [6]. These different values for the silicon dioxide parameters result solely from changing the assumed silicon optical constants used in the analysis. The range of silicon optical constants shown in the figure are based on the values found in published literature [8]. The results obtained using the particular values of silicon optical constants cited in ASTM Method F-576 [7] are also indicated in the figure. While it is probable that most of the scatter in the reported silicon optical constants is due to measurement uncertainty, it is also possible that residual silicon lattice damage, whether from silicon slice preparation or from such processing steps as ion implantation [9], inherently controls the optical constants at the surface of the silicon to some degree. If this is the case, no single set of silicon optical constants would be exactly applicable to all silicon specimens and a unique and accurate transfer of oxide thickness scale by use of an SRM would not be possible via ellipsometry (or any other optical technique which utilizes reflection from the unmetallized and transparent dielectric layer). Further, it is unclear whether the silicon optical constants measured at 632.8 nm have the same relative error as the optical constants at 546.1 nm (the other wavelength commonly used for ellipsometry).

In light of the foregoing comments, it is useful to consider the advantages as well as the risks and limitations encountered when attempting to obtain both accuracy and uniformity in thin film measurements through using reference specimens. To do this, it is helpful to assume that several known sources of measurement error have been eliminated. Assume first that the reference specimen is absolutely uniform laterally so that any region measured will provide the same measurement values as any other. Next, assume the specimen to be stable; this requires both suitable temperature control and a means for contamination-free storage or a means for removing all contamination prior to measurement. Then assume all instrumentation errors can be eliminated or accounted for. With an ellipsometer this means, for example, that the system can be aligned accurately at the angle of incidence used for data analysis and that the deviations from ideal behavior found in optical components, such as the compensator, are nonexistent or can be accounted for. Finally, for successful transfer of the SRM to the user's ellipsometer, assume it is possible to insert the same values for the silicon optical constants into the user's ellipsometry analysis as were used for certification of the reference material. These assumptions may not be fully realizable in practice, for example, the last may not be possible for automated ellipsometers. Failure to meet the assumptions will variously cause loss of precision or accuracy when using the reference specimen to transfer the measurement scale.

It is now necessary to ask what is really needed from the reference material. Should it be characterized for the absolute thickness of the silicon dioxide layer and of the transition layer (taken separately) or for the effective thickness of the total dielectric layer (taken as a single layer)? The choice made may make only a small difference in thickness value for nominal 100-nm layers, but it may result in significant differences for layers on the order of only a few tens of nanometers thick.

If all further use of reference material will be restricted to ellipsometry measurements in laboratory applications, the primary application will probab-

ly be to materials research. In this case, that the thickness of the silicon dioxide and transition layer should be separately specified, with stated values having been corrected for strain and other known effects. However, if the application of the reference material is to routine monitoring of a product line via ellipsometry, this latter characterization of the reference material may well be counterproductive. In such a case, one probably does not make corrections for strain of the product wafers, nor does one want to know the thickness of the silicon dioxide and transition layers separately. Product layers are likely to be characterized for total effective dielectric thickness, with the reference material being used to test the ability of the instrument to faithfully transfer a scale for total effective dielectric thickness. The reference material is then best certified only for total effective dielectric layer thickness.

While this latter simplified form of reference material characterization is probably acceptable for applications restricted to ellipsometry, it must be realized that it is a step in the wrong direction if one wishes to improve the uniformity of measurement scales between ellipsometers, spectral reflectance instruments, and surface profilometers. In the case of spectral reflectance instruments now used for film thickness measurements, the algorithms used to calculate layer thicknesses are proprietary. The differences in thickness values often experienced between these instruments and ellipsometers may be due to differences in the silicon optical constants used in the measurement analyses, to differences in the way the transition layer affects the measurements, to the quality of the analysis algorithms, or to some combination of these effects. In any case, little help can be expected in reducing this discrepancy if the reference material is characterized only by a simple effective thickness, since this may not provide enough information to aid in sorting out the source of the discrepancy.

Similar difficulties arise if one tries to improve the agreement in measurement values between ellipsometers and surface profilometers and uses SRMs characterized only for total effective layer thickness. (It is recognized that surface profilometers are not likely to be used for measuring silicon dioxide layers because bare silicon oxidizes slightly in room ambient, and hence a window etched through the silicon dioxide to the underlying silicon surface for stylus measurements will not maintain a stable absolute base line.) Nevertheless, the sense of the problem can be described for the case of a single silicon dioxide layer over silicon. Here, the thickness scale conveyed by an ellipsometrically measured, total effective layer thickness may not be the same as the total optical thickness evaluated by more sophisticated modeling of the transition region. The simple total effective thickness simply cannot be expected to be the same as the total mechanical thickness of the layer (measured by profilometer) for arbitrary shapes and thickness of transition layers produced by a variety of CVD or thermal processes. The additional complications already noted for a multiple layer structure further degrade the level of measurement scale accuracy and uniformity which can be transferred through the use of reference materials.

It is useful to put some of these comments in perspective. A detailed characterization of the total dielectric layer and its structure appears to be possible using spectral ellipsometry or by single wavelength ellipsometry using sequential etching and measurement steps to characterize the process by

which the SRM was fabricated. The price paid for this additional information on a reference artifact is cost of the reference specimen to the user. At present, the errors in thickness value likely to be encountered by treating the silicon dioxide as completely uniform and strain free are quite small for thermally oxidized nominal 100-nm specimens, and perhaps can be ignored, at least for ellipsometry applications. It is not known, however, how well the measurement scale conveyed by an SRM characterized in this manner can be transferred to other types of oxide thickness measurements, or to oxides formed by CVD or anodic processes. Further, as technology pushes toward 20-nm layer thickness, all such material effects, if unaccounted for, will become serious limits on the effectiveness of reference materials for improving the uniformity and accuracy of thin film measurements.

SUMMARY

Although, methods exist which can make film thickness measurements with excellent resolution and precision, their absolute accuracies are not well defined. Aside from errors due to specimen instability, inherent limits are imposed by what is known, and not known, about "real world" thin films on silicon and the silicon itself. Reference specimens can be certified by a technique which is well documented, such as ellipsometry, but their valid use is best restricted to ellipsometric applications. Meaningful improvement upon such an approach will require an active investigation of the accuracies and limits of error obtainable with other thickness measuring techniques, with accuracies being traced to fundamental atomic or wavelength standards. Also important for meaningful improvement is the need for active dialogue between the semiconductor industry and NBS. This is necessary to establish the intended applications, the range of values required and the accuracy and precision needed from film thickness SRMs. This information can then be used to select reference material characterization procedures which will best effect overall improvement in thin film metrology.

REFERENCES

1. Uriano, G., and Gravatt, C. C., The Role of Reference Materials and Reference Methods in Chemical Analysis, *CRC Crit. Rev. in Anal. Chem.* 7, 362-411 (1977).

2. *1979 Annual Book of ASTM Standards,* The American Society for Testing and Materials, Philadelphia, Pennsylvania.

3. See, for example, Helms, C. R., Johnson, N. M., Schwarz, S. A., and Spicer, W. E., Auger Sputter Profiling Studies of the Si-SiO_2 Interface, *The Physics of SiO_2 and Its Interfaces,* S. T. Pantelides, Ed., pp. 366-372 (Pergamon Press, New York, 1978).

4. Taft, E., and Cordes, L., Optical Evidence for a Silicon-Silicon Dioxide Interlayer, *J. Electrochem. Soc.* 126, 131-134 (1979).

5. Azzam, R. M. A., and Bashara, N. M., *Ellipsometry and Polarized Light* (North Holland Publishing Co., Amsterdam, 1977), pp. 364-415.

6. McCrackin, F. L., A FORTRAN Program for Analysis of Ellipsometer Measurements, NBS Technical Note 479 (April 1969).

7. Standard Method for Measurement of Insulator Thickness and Refractive Index on Silicon Substrates by Ellipsometry, ASTM Designation F 576, *Annual Book of ASTM Standards,* Part 43 (November 1979).

8. Algazin, Y. B., Blyumkina, Y. A., Grebnev, N. I., Svitashev, K. K., Semenenko, L. V., and Yablontseva, T. M., Optical Constants and Temperature Dependences of Atomically Pure Surfaces of Germanium and Silicon, *Opt. Spectrosc. (USSR)* 45, 183-188 (1978).

9. Watanabe, K., Miyao, M., Takemoto, I., and Hashimoto, N., Ellipsometric Study of Silicon Implanted with Boron Ions in Low Doses, *Appl. Phys. Lett.* 34, 518-519 (1979).

APPENDIX

STABILITY OF SILICON DIOXIDE LAYER THICKNESS IN SIMPLE STORAGE ENVIRONMENTS

A study was made of the temporal stability of thermally grown silicon dioxide layers which could be obtained with simple storage procedures. Twenty-eight wafers of nominal 50-nm oxide thickness and 28 wafers of nominal 100-nm oxide thickness were used in this test. For each thickness the wafers were subdivided into seven sets of four wafers each. One set (of four wafers) of each thickness was assigned to each of seven storage procedures. Five of the storage procedures utilized glass desiccator storage with environments consisting of 1) house vacuum, 2) dry nitrogen back-fill, 3) polypropylene wafer packages in dry nitrogen ambient, 4) 80-percent relative humidity (RH) maintained by a glycerin-water mixture, and 5) 80-percent RH maintained by an aqueous potassium bromide solution. The two remaining storage procedures were: 6) open glass rack mounting in a class 100 laminar flow hood, and 7) open glass rack mounting in office environment. All wafers were measured ellipsometrically immediately after fabrication and at irregular intervals during the ensuing year. Figures A-1 and A-2 summarize the behavior of the average (of four) thickness values as a function of time, and show a continual increase in thickness throughout the storage time. (The wafers stored in office environment rapidly moved off the scale of this plot and are not shown.) At the end of the one-year storage, each set of four wafers was divided into two subsets of two wafers each.

Each of the subsets was assigned to one of two cleaning procedures. The first consisted of 10 min in hot trichloroethylene, followed by successive rinsing with acetone, methanol, deionized water, and drying in flowing nitrogen; the second consisted of 10 min in a solution of ammonium persulfate in sulfuric acid at approximately 100°C followed by rinsing in deionized water and drying in flowing nitrogen. (Both cleaning procedures had been pretested on freshly oxidized wafers to ensure that there was no attack of the oxide itself.) The average thickness decrease of any subset following one cleaning procedure was not always the same as that resulting from the other cleaning procedure on the companion subset, and no systematic difference between the cleaning procedures could be identified. The final post-cleaning thickness values shown at the extreme right of the figures are the combined results from the two procedures.

If data for the two thicknesses are carefully compared for certain storage conditions, there appear to be some inconsistencies in the relative thickness changes experienced. These inconsistencies may not be statistically significant, however, since an estimate of the standard deviation for the overall measurement process is 0.25 percent. Nevertheless, some basic conclusions can be drawn. First, it was not generally possible, after cleaning, to return exactly to the initial values of thickness. Next, both cleaning procedures were reasonably effective in reducing the long-term increase in specimen thickness. Excluding specimens stored in either of the open exposure environments, the residual thickness increases (post-cleaning thickness minus initial thickness) were in the range 0.2 to 0.5 nm. This offset, while less than a monolayer for stoichiometric silicon dioxide, must be considered as a

limitation on the accuracy with which a thickness scale can be transferred using silicon dioxide SRMs with reasonably simple storage procedures.

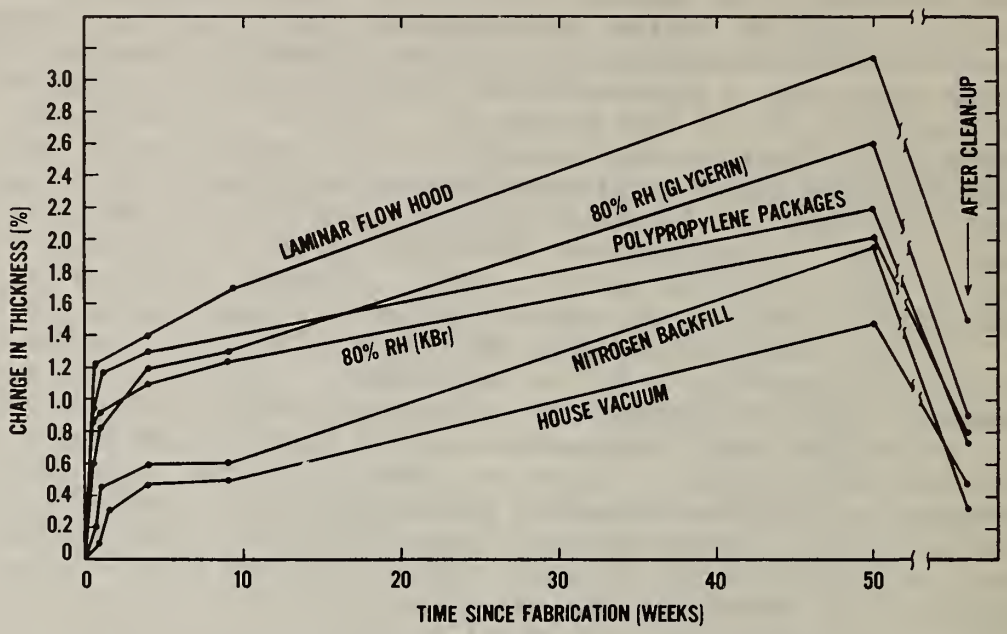

Figure A-1. Change of thickness of nominal 50-nm silicon dioxide layers *versus* time for several storage conditions.

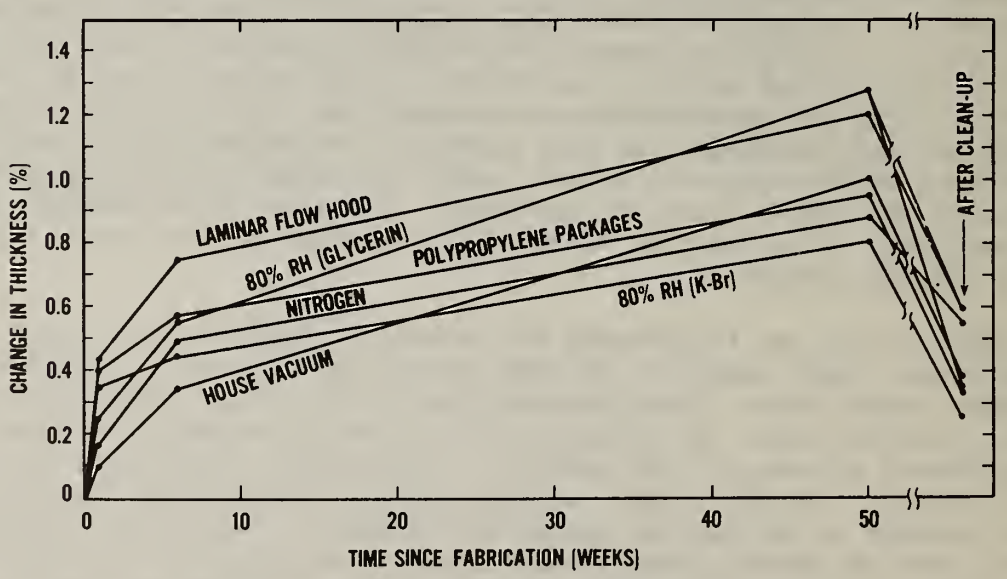

Figure A-2. Change of thickness of nominal 100-nm silicon dioxide layers *versus* time for several storage conditions.

NBS-114A (REV. 2-8C)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET (See instructions)	1. PUBLICATION OR REPORT NO. NBSIR 80-2158	2. Performing Organ. Report No.	3. Publication Date November 1980

4. TITLE AND SUBTITLE

Some Considerations Regarding Film Thickness Standards for the Semiconductor Industry

5. AUTHOR(S)

James R. Ehrstein

6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions)

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP)

National Bureau of Standards
Department of Commerce
Washington, DC 20234

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

Semiconductor integrated circuit manufacturing has witnessed a rapid evolution of processing techniques and a reduction of structural dimensions. This has placed a great burden on metrology for process development and for process monitoring, both because of the smallness of the dimensions involved and the variety of interferences encountered in measuring differing structural combinations of thin films. One possible means for improving the uniformity and control of semiconductor thin film measurement would be through the use of certified thickness standards, such as have been requested of the Standard Reference Material Program at the National Bureau of Standards.

This paper will first consider some of the requisite properties of Standard Reference Materials (SRMs) for effective use in improving the uniformity of measurements. It will then consider some of the limitations imposed by real-world thin film specimens and our state of understanding of their properties as well as by the different types of measurements available. Finally, the need for improved measurement control will be related to the SRM program in light of these limitations.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

Ellipsometry; polysilicon films; Standard Reference Materials; silicon dioxide films; silicon nitride films; thin films.

13. AVAILABILITY

☒ Unlimited

☐ For Official Distribution. Do Not Release to NTIS

☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

☐ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES

15. Price